

## LOW-SEVERITY COAL LIQUEFACTION A CHALLENGE TO COAL STRUCTURE DEPENDENCY

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### INTRODUCTION

The purpose of this paper is to summarize recent information from coal liquefaction studies in bench scale as well as in integrated process development units, together with the data from new analytical techniques which have provided substantial amounts of new information on several important aspects of coal structure and coal reactivity. The results of these studies reveal that existing coal models and current empirical tests for coal reactivity no longer reflect adequately the new knowledge of coal structure and coal reactivity.

Earlier approaches to direct coal liquefaction employed high-severity operating conditions of pressure, temperature and coal/solvent slurry contact time, to achieve in one reactor the highest coal conversion and distillate yield possible. High-severity thermal processing did not necessarily lead to reactions that were all desirable, but resulted in undesirable regression reactions, such as polymerization, condensation and an increase in the aromatic nature of the initially-formed coal fragments. Although elevated temperatures may be necessary for the breakdown of the original coal structure, preventive means, such as a kinetically rapid hydrogen transfer from a hydrogen donor solvent to stabilize the overall solvent-coal adduct, have been employed to mitigate the regressive reactions. However, because of lack of sufficient transferable hydrogen to maximize the conversion of the asphaltols and asphaltenes, which contain highly reactive functional groups, polymerization/condensation and dealkylation reactions still occur, as evidenced by high hydrocarbon gas yield.

### DISCUSSION

The key role of the functional groups, and in particular of the phenols, in promoting and participating in polymerization/condensation reactions is well established (1). But the seemingly important function of the aliphatic groups attached to the aromatic structure of the coal and of the donor solvent is that of forming free radicals at high thermal severity, competing kinetically and taking away the available hydrogen directed to the condensed aromatic structure, which eventually goes to coke or insoluble organic matter. The fate of the aliphatic groups in coals and those formed by cracking hydrogenated aromatic rings during upgrading of the coal extracts, has not been sufficiently studied, particularly in relation to their key role in coal liquefaction. High thermal severity coal liquefaction processes, which have monopolized bench scale research and scale-up efforts from the early German discoveries to the present time, seem to have a pronounced dependency on coal structure somewhat similar to those of coal gasification and combustion, since all of these are operating above the activation energies of all the major reactions involved and are dominated by an unordered

retrogressive condensation, cracking and transalkylation array of reactions. For these and other reasons the organic structure of coal has appeared to researchers as a highly crosslinked, amorphous and unreactive macro-molecular structure.

A more recent approach uses low-severity coal liquefaction in separated but integrated stages in order to optimize the coal dissolution and coal extract upgrading steps (2). This emerging technology and the development of new analytical techniques have produced results which change substantially our approach to coal liquefaction techniques, have inspired new thoughts in unraveling the complex mechanism of direct coal liquefaction at low-severity and more importantly give us a radically different picture of the structure and reactivity of coals than has been provided by high-severity liquefaction, gasification and combustion processes.

Important new information from this new approach includes:

- o Low-severity processing forms mostly reactive low molecular-weight fragments. If not properly quenched, these reactive fragments, which are formed in the very early stages of liquefaction, can condense to form structures similar to those produced by high-severity liquefaction (3).
- o Thermally produced coal extracts contain high levels of heteroatom compounds and are "refractory" to catalytic hydrogenation. Conversely low-severity produced extracts are low in heteroatoms and more easily hydrogenatable, and consistently yield excellent equilibrium hydrogen donor solvent (4).
- o Perhaps because of the occurrence of low molecular-weight reactive coal fragments, surrounded by a recycle solvent which is low in heteroatoms and rich in hydroaromatics, this approach appears to be successful in processing both high- and low-reactivity coals, and producing similar conversions and similar product qualities from both types of coal, supporting the notion that conversion and product quality is less dependent on coal characteristics and more dependent on process operation than previously believed (4).
- o Proton NMR analysis, modified to provide data on distillate and non-distillate fractions, served to create a working kinetic model for coal extract hydroprocessing, thus enabling us to distinguish catalytic hydrogenation from ring opening and particularly from dealkylation of the highly alkylated condensed hydroaromatic compounds produced by low-severity liquefaction, and to predict solvent donor quality as well as the yield structure of the upgraded products (5).

Other important information has been obtained by various sources working at low-severity process conditions, but this information is mostly related to operability advantages, since processing was the main objective of the projects involved. Nevertheless, the limited information given here appears to disclose a completely different picture of the relationship between the structure and reactivity of coals and low-severity coal liquefaction.

We are discovering more similarities in coal-derived products even though there are large differences in the structure of the coals from which these products are derived. These similarities become more evident as the coal/solvent donor slurry is processed at controlled low-severity in the extraction as well as in the upgrading steps under the conditions where equilibrium is more closely reached and in the presence of an aged catalyst with steady-state activity.

It is extremely difficult to capture in research bench scale units the essence of the results produced in an integrated continuous process because the rapid initial deactivation of fresh catalyst provides continuously changing conditions leading to rather confusing results. Also, most of the key data and benefits, i.e., increased coal conversion, enhanced donor quality, and increased formation of few major condensed hydroaromatic compounds, are obtained only after several cycles of the integrated continuous staged operation. At process equilibrium, benzopyrenes, phenanthrenes and chrysenes and their highly alkylated derivatives constitute more than 60 percent of the total product, whether a bituminous or a subbituminous coal is employed as the starting material (6).

#### R&D COORDINATION

Current research efforts on coal liquefaction are leading to further improvement in the understanding of the mechanism of reactions occurring at even lower temperatures and overall less severe processing conditions, revealing that coal, asphaltols and asphaltenes are much more reactive species than previously thought. It can be stated that there is a turn of events occurring in direct coal liquefaction, which from a steady evolutionary progress, has recently become a revolutionary processing approach. Preliminary results indicate that this approach will provide a much larger "equalizer" effect on processing any type of coal, making it even more process dependent rather than coal type dependent (7).

On the basis of the above new information, evidently there is an urgent need for in-depth discussion between researchers who are dedicated to unravelling coal characteristics, mechanisms and reactivities and those who are devoted to coal processing and the kinetic aspects of the reactions involved in each phase of the low-severity coal liquefaction process.

Due to changing economics, the introduction of new large-scale coal conversion processes has been postponed and, as a consequence, more time is available for research to gain fundamental insights into coal structure and to obtain a better understanding of its impact on coal liquefaction.

Therefore, the recent exciting results obtained in the development of an emerging technology in direct coal liquefaction should be discussed, possibly in small-scale symposia, as a supplement to the large-scale conferences, i.e., ACS, AIChE, Contractors' and Coal Science Conferences and thus provide the opportunity for in-depth discussions and a maximum profit from exchange of knowledge and ideas, and better utilization of research talents and dollars.

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